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Electric field gradients in nanoparticles of $HfAl_2$ and $HfAl_3$ intermetallic compounds

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Abstract Perturbed angular correlation (PAC) method was applied to study the electric field gradients in nanopowders of the $HfAl_2$ and $HfAl_3$ intermetallic compounds, obtained via mechanical alloying or after ball milling of the thermally alloyed compound. The influence of the ball milling procedure on the experimentally obtained hyperfine interaction parameters was determined. A strong dependence of the PAC pattern on the milling time was evidenced and attributed to the structural disorder. The thickness of the outer damaged part of the grains depends on the crystallographic structure of the milled material. In $HfAl_3$ sample the influence of the milling procedure on the phase transformation was observed.

Keywords Ball milling · Hf-Al compounds · Hyperfine interactions · TDPAC

1 Introduction

Mechanical alloying, a dry and high-energy milling process, is a method of synthesis of materials, alloys of immiscible elements, amorphous phase and all sorts of compounds and composites. Almost all kinds of solids may be synthesized or transformed by high-energy-milling. Nanostructured materials have, in most cases, a large fraction of atoms residing in defect environments. The fraction of atoms situated in the defected grain boundary region depends directly on the grain size. According to Van Swygenhoven et al. [1] the volume fraction associated with grain boundaries is of ∼20% for a grain boundary thickness of ∼0.7 nm and a grain size of 10 nm. The characterization of nanocrystalline materials is performed by a multitude of different techniques well known in material sciences. However, there is an obvious need for

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techniques that possess short range sensitivities like nuclear hyperfine interaction methods.

Here we present an attempt to follow the changes of the hyperfine interaction parameters obtained in PAC experiments for $^{181}Hf/^{181}Ta$ probes in the ball milled $HfAl_2$ and $HfAl_3$ compounds. In particular, it was our aim to determine how the EFG parameters are influenced by the grain dimensions.

2 Experimental details

Mechanical alloying technique was used to synthesize the $HfAl_2$ sample. The elemental powders of aluminum and hafnium were used as starting materials and mixed to yield $Hf_{33}Al_{67}$ composition. Then placed in a planetary mill and milled at room temperature to get $HfAl_2$ alloy. In order to performed the PAC measurements on $^{181}Hf/^{181}Ta$ probes a suitable amount of the same powder was sealed under high vacuum in a quartz ampoule and irradiated with neutrons at a flux of 10^{14} neutrons/cm^{2}s in the pile of the Świerk reactor MARIA.

In addition, the $HfAl_2$ and $HfAl_3$ bulk compounds, of C14 and $D0_{23}$ types of structures, respectively [2], were prepared by multiple arc melting (under argon atmosphere) of the appropriate amounts of high purity constituents of the alloys and a small amount of neutron irradiated hafnium. After such procedure, the $HfAl_2$ and $HfAl_3$ samples contained 33.0 and 24.9 at.% hafnium, respectively.

Then both samples have been mechanically ground using a high-energy ball mill SPEX 8000 equipped with the acrylic vial and two 0.25 in.-diameter tungsten carbide balls. To prevent contamination from the atmosphere, all the powder preparations were performed under Ar atmosphere. Powdering of the bulk sample was performed successively and after each step the PAC measurement was executed at room temperature. Details of the PAC apparatus used and data analysis have been reported previously [3, 4]. After some of the milling steps, a part of the same sample was analyzed in the XRD experiment to follow the evolution of the crystal structure and of the grain dimensions.

3 Results and discussion

3.1 PAC and XRD measurements for mechanically alloyed $HfAl_2$ compound

The grain size of the mechanically alloyed $HfAl_2$ sample reached a mean value of ca. 65 nm. The PAC spectrum taken directly after irradiation, exhibited only a broad distribution of the EFG without any signal from the stoichiometric Hf-Al phases. Successive annealing of powder in vacuum up to 900°C executed in order to remove the possible defects caused by the milling procedure did not improve the PAC signal (see Fig. 1).

In XRD analysis, the as prepared sample exhibited the reflexes of $HfAl_2$ phase, and also one could identify signals from the Hf_2Al_3 and $HfAl_3$ admixtures (Fig. 2b). In the annealed sample, the obtained spectrum exhibited mainly reflexes characteristic for the C14 structure of $HfAl_2$ compound (see Fig. 2c). All three hafnium aluminides mentioned above were already the subject of our former PAC

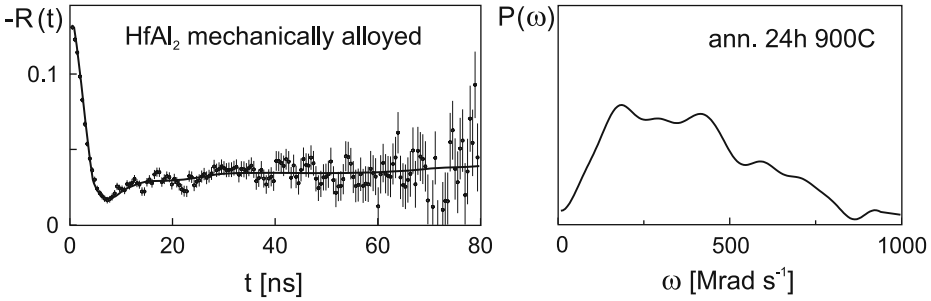

Fig. 1 PAC spectrum with Fourier transform of the mechanically alloyed $HfAl_2$ compound after annealing up to 900°C

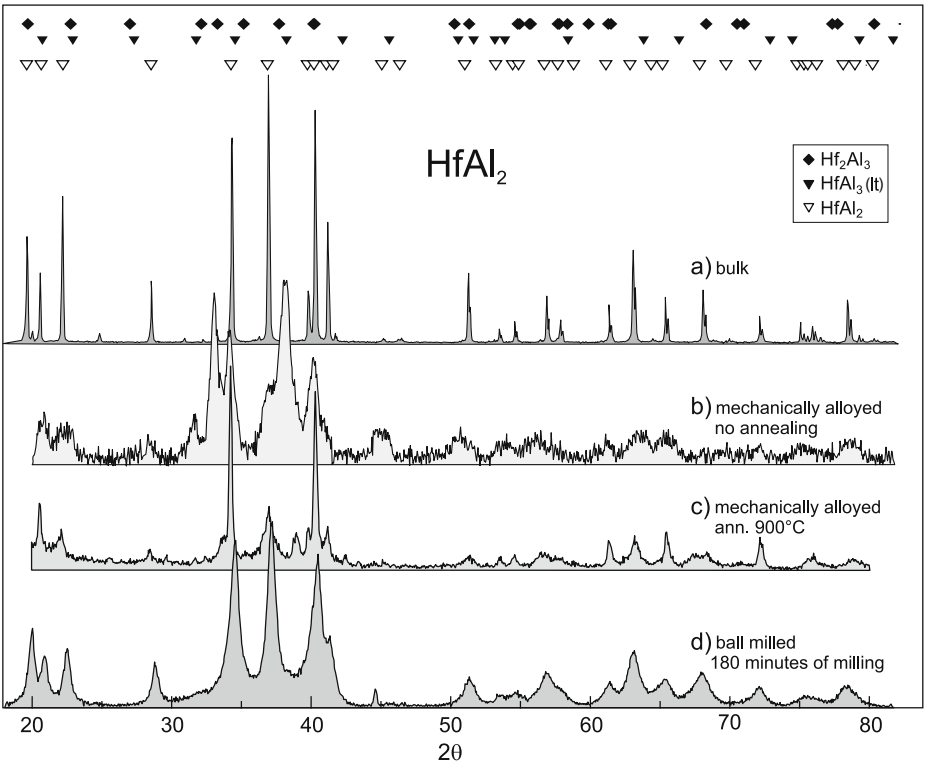

Fig. 2 XRD spectra of $HfAl_2$ **a** bulk sample; **b** as prepared mechanically alloyed powder; **c** mechanically alloyed sample after annealing at 900°C; **d** ball milled sample. Lines corresponding to the $HfAl_2$, $HfAl_3$ (lt) and Hf_2Al_3 standards are marked as indicated

investigations, therefore, the EFG parameters for the ^{181}Ta probes in these lattices are well known [3–5]. Thus, in the PAC measurement for the mechanically alloyed $HfAl_2$ sample each of them should be easily identified.

Such different results of XRD and PAC measurements led us to conclusion that the grains of $HfAl_2$ nanopowder are too damaged to exhibit a clear electric field

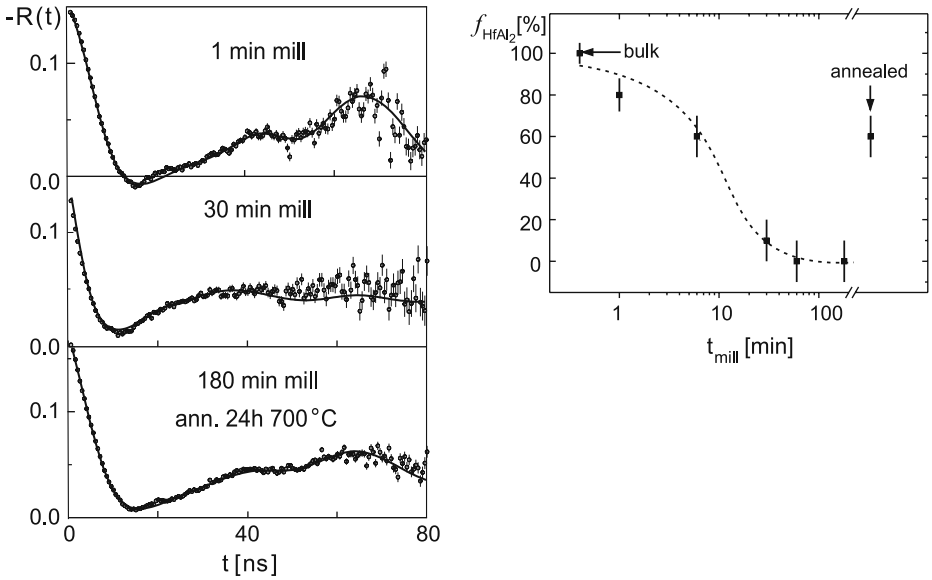

Fig. 3 *Left panel* PAC spectra for ball milled $HfAl_2$ sample taken after 1, 30 min of milling and after 180 min with additional annealing at 700°C. *Right panel* Evolution of the probe fraction in undamaged $HfAl_2$ structure during milling

gradient value acting on the probe atoms. In order to confirm this statement and to determine the limit dimension of the sample particles for the clear PAC signal we decided to make another experiment, in which the bulk $HfAl_2$ sample was successively ground in a ball mill.

3.2 Ball milling of the bulk $HfAl_2$ compound

The X-ray diffraction pattern of the bulk $HfAl_2$sample confirmed the C14-type structure of the investigated sample without admixture of the other phases (Fig. 2a). Then, the sample was successively milled for 1, 6, 30, 60 and 180 min (total times of milling). After the last two milling steps the powder was analyzed in XRD experiment. Basing on the broadening of the X-ray diffraction peaks [6], the average grain sizes determined by the Debye-Sherer formula achieved ca. 29(3) nm and 26(3) nm for 60 and 180 minutes of milling, respectively. The corresponding XRD spectrum taken after $t_{mil} = 180$ min is presented in Fig. 2d.

The PAC spectra taken for the ball milled $HfAl_2$ sample after 1, 30 and 180 minutes of milling (the last after additional annealing at 700°C) are presented in Fig. 3 (left panel). The right panel of Fig. 3 illustrates the evolution of probe fraction in undamaged $HfAl_2$ structure. Due to the milling procedure this fraction successively decreases while the width of the EFG distribution increases. After 6 minutes of milling ca. 60% of the grain volume is still not damaged, while after 60 minutes the whole volume of grains is defected and only a broad distribution of the quadrupole frequencies around the value typical for the bulk $HfAl_2$ sample is observed.

Table 1 Quadrupole interaction parameters for ^{181}Ta in $HfAl_2$ and $HfAl_3$ compounds

Phase	Structure	ν_Q(MHz)	$\lvert V_{zz}\rvert$ (10^{17} Vcm^{-2})	η	Ref.
$HfAl_2$	C14	97(1)	1.7(2)	0	[4]
$HfAl_3$ (lt)	$D0_{23}$	355(1)	6.22(2)	0	[3]
$HfAl_3$ (ht)	$D0_{22}$	713(2)	12.49(2)	0	This work

The results of both – PAC and XRD experiments led us to conclude that the EFG value acting on the radioactive probe atoms in ball milled $HfAl_2$ powder is not well defined when the crystallite size is below ca. 30 nm. This limit size is certainly somewhat larger than 30 nm but lack of the XRD analysis after 30 minutes of milling did not allow us to determine this value more precisely. Above this size it is possible to distinguish between (1) the grain-boundary phase with mechanically damaged structure, described by a large quadrupole frequency distribution, and (2) the not or less damaged region with EFG corresponding to the value typical for $HfAl_2$ phase (see Table 1). It should be noticed that the damaged structure from the PAC point of view does not prevent obtaining a clear XRD signal typical for the crystalline phase.

In order to check that the defects at the grain boundaries are responsible for the largely distributed EFG we annealed the $HfAl_2$ powder, formerly milled for 180 minutes, at 700°C for 24 hours. The evidenced change of the PAC pattern (lowest panel of Fig. 3) proves that the defects in the crystal structure have been partially removed during the annealing and the frequency distribution became close to that for the not milled sample. The fact that the annealing procedure did not repair the $HfAl_2$ structure in the whole volume fraction points to a significant structural disorder in the outer part of grains.

3.3 Ball milling of the bulk $HfAl_3$ compound

$HfAl_3$ intermetallic phase crystallizes in the $D0_{23}$ structure (its low temperature (*lt*) phase), while the crystal structure of its high temperature (*ht*) phase is of $D0_{22}$type [2]. This *ht* phase is reported to be stable between 700°C and 950°C [7]. The hyperfine interaction parameters for ^{181}Hf/^{181}Ta probes placed in the low temperature phase were reported in Ref. [3] (Table 1). In the experiments presented here the $HfAl_3$ bulk sample was successively milled for 5, 10, 20, 30 and 60 min (total times of milling). PAC and XRD spectra were taken for the bulk sample and after each step of milling.

The PAC spectrum for the bulk sample exhibited two EFG's. One of them of dominant contribution (ca. 60%), has the EFG typical for the *lt* phase ($D0_{23}$) [3]. Second one is attributed to the *ht* phase ($D0_{22}$), which was created as the consequence of the arc melting followed by a fast cooling down to the room temperature.

Evolution of the PAC spectra with the increasing milling time is presented in Fig. 4. It is clearly seen that the distribution of the both EFG's increases systematically with rise of the milling time. Annealing of the $HfAl_3$ powder, performed at the end of the milling procedure, at 500°C led to a PAC spectrum with well defined quadrupole frequency typical for the low temperature $HfAl_3$ phase (Fig. 4 lowest panel). Lack of the high temperature phase (which was observed before the milling program) proves that the defects in the crystal structure created during milling facilitated the recrystallization of the sample in the low temperature phase. Additional annealing at 900°C followed by a fast cooling down caused again

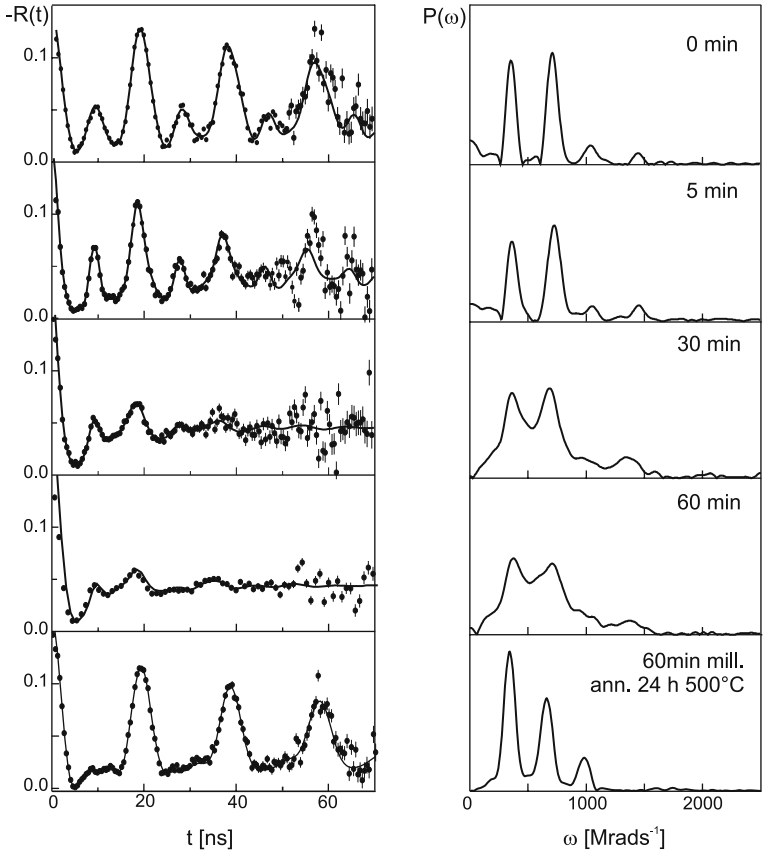

Fig. 4 Sequence of the PAC spectra and the corresponding Fourier transforms taken after successive milling and annealing of the ball milled $HfAl_3$ sample

the formation of a small fraction (ca. 20%) of the *ht* phase. This observation is in agreement with the experimental [8] and theoretical [9] data on the phase transition temperature—650°C—between phases of $D0_{22}$ and $D0_{23}$ structures. The presence of both phases in the milled sample was confirmed in the XRD analysis (see Fig. 5).

Influence of the milling time on the *hfi* parameters and the grain size illustrates Fig. 6. The PAC signal, typical for the amorphous structure, is presented by only ca. 30% of probes after 30 min of milling, while the rest of probe atoms are placed in a less damaged environment. The fraction of the high temperature phase decreases upon milling time in favour of the amorphous phase. The width δ of the EFG distribution corresponding to the *lt* phase increase up to 18(2)%, while in the *ht* phase only up to 7(1)%. The grain size of both structures decrease to about 30 nm after 30 min of milling. For the *lt* phase the grain size did not reduced significant after 60 min of milling. The determination of the grain size for the *ht* phase was not possible due to the peak broadening and overlapping of the peaks attributed to both phases.

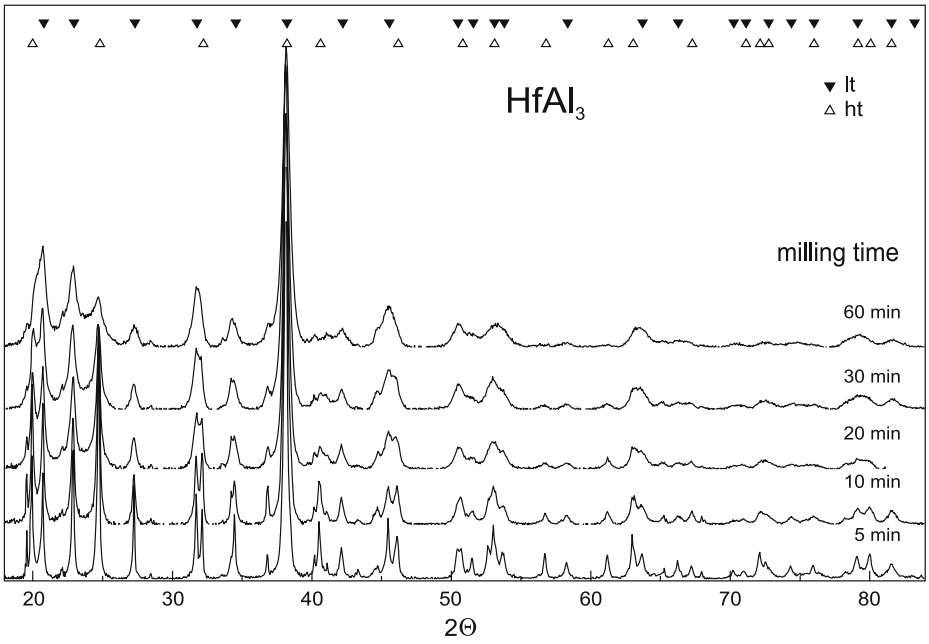

Fig. 5 XRD spectra for $HfAl_3$ sample measured after each milling step. Peaks of the low and high temperature phases are indicated

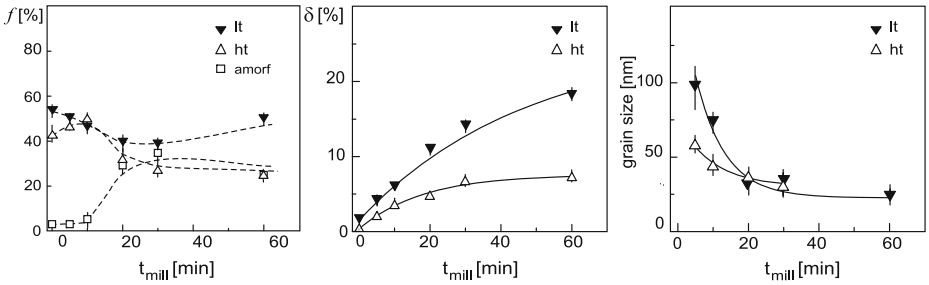

Fig. 6 Influence of the milling time on the observed EFG fractions, frequency distribution widths, and average grain size in $HfAl_3$ sample

4 Conclusions

Experiments with mechanical alloying described in Section 3.1 demonstrated, that such process causes more serious and stable damage in the powder particles than grinding of the formerly alloyed sample. In the case of mechanical alloyed sample, even larger size of grains (ca. 65 nm) is not sufficient for the well-defined EFG. Moreover, annealing up to 900°C was not sufficient to remove these defects.

It has been shown that (for formerly melted $HfAl_2$ bulk sample) during the milling procedure the relative sample volume with damaged crystal structure continuously increases up to 100% when the average crystallite size is not smaller than ca. 30 nm.

These structural defects can be only partially removed via annealing at elevated temperature.

In case of small grains the disordered grain-boundary region is so wide that 100% of probe atoms are placed in it, while the XRD spectrum still exhibits the $HfAl_2$ pattern. This fact seems to indicate that at least the inner part of powder grains have a not completely disordered structure but rather a damaged structure, similar to that in microcrystals. On the other hand, the presence of the wide grain boundaries with disordered structure to the extent that it lacks even the short-range order of an amorphous phase, described by the Gleiter model [10], is not excluded, as after the annealing procedure only a part of probe atoms exhibits the EFG value typical for crystalline $HfAl_2$ phase. Our results corroborate those of Wichert et al. for different semiconductors and alloys [11] and support those models which assume a separate grain-boundary phase with distorted structure.

The results for $HfAl_3$ sample confirm that the milling procedure introduces a serious damage of the compound structure, which in this case can be removed by the annealing. The observed quadrupole frequencies were less distributed than for $HfAl_2$ sample, in spite of the even smaller grain sizes. This finding indicates that the thickness of the outer damaged part of grains depends on the crystallographic structure of the milled material.

Comparison of the PAC results for milled and not milled samples annealed at 500°C illustrates how the milling procedure can enable a phase transformation in $HfAl_3$ compound. Experimental techniques characterized by the short range sensitivities, like nuclear hyperfine interaction methods, deliver separate information about crystallites and grain boundaries of the investigated materials.

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